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Low Temperature N_2 Binding to 2-coordinate L_2Fe^0 Enables Reductive Trapping of $L_2FeN_2^-$ and NH_3 Generation.**

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Abstract

The 2-coordinate $(CAAC)_2Fe$ complex [CAAC = cyclic (alkyl)(amino)carbene] binds dinitrogen at low temperature (T < −80 °C). The resulting putative 3-coordinate N_2-complex, $(CAAC)_2Fe(N_2)$, was trapped by one electron reduction to its corresponding anion $[(CAAC)_2FeN_2]^-$ at low temperature. This complex was structurally characterized and features an activated dinitrogen unit that can be silylated at the β-nitrogen. The redox linked complexes $(CAAC)_2Fe^{I}BAr^{F}_{24}$, $(CAAC)_2Fe^0$ and $[(CAAC)_2Fe^{-I}N_2]^-$ were all found to be active for the reduction of dinitrogen to ammonia upon treatment with reductant (KC_8) and acid ($HBAr^{F}_{24}{\cdot}2Et_2O$) at −95 °C (up to 3.4 ±1.0 equivalent of ammonia per Fe center). The N_2 reduction activity is highly temperature dependent, with significant N_2 reduction to NH_3 only occurring below −78 °C. This reactivity profile tracks with the low temperatures needed for N_2 binding and an otherwise unavailable electron transfer step to generate reactive $[(CAAC)_2FeN_2]^-$.

Keywords

Iron; Nitrogen fixation; Low-coordinate; Carbenes

While hundreds of transition-metal-N_2 complexes have been prepared and studied,[1] comparatively few systems afford access to productive N_2 functionalization.[2] This is particularly true for the case of N_2 functionalization by protons and electrons to produce NH_3 (or N_2H_4). Building on extensive early Mo and W model work,[3] Schrock[4] and Nishibayashi[5] have reported Mo-containing coordination complexes (**A** and **B** in Figure 1, respectively) that facilitate catalytic N_2 reduction to NH_3 in the presence of suitable acids and reductants. Because Fe is (i) the only transition metal known to be essential to enzymatic nitrogenase function,[6] and (ii) the predominant transition metal catalyst used in the Haber-Bosch ammonia synthesis,[7] studying N_2 reduction chemistry at well-defined Fe model complexes is of interest.[8,9] Recently, our lab demonstrated that Fe coordination complexes (**C** in Figure 1) are capable of modest catalytic N_2 reduction to NH_3.[10]

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The functional Fe-N_2 reduction systems we have studied to date are phosphine supported 5-coordinate XL_3Fe-N_2 adducts. It is of interest to explore whether other donor ligands and geometries might expose similar reactivity patterns for Fe-N_2 species.[11,12] For example, Holland and co-workers recently reported a solution characterization of a 3-coordinate Fe complex with an N_2 ligand linearly bridged between Fe and a solvated Mg cation (**D** in Figure 1).[13,14] The N_2 ligand in this complex is highly activated. However, only trace NH_3 (< 2% per Fe) could be detected upon attempts to mediate its reductive protonation. Related low-coordinate Fe-N_2 species can undergo reductive N_2 cleavage which, when followed by a separate acidic work-up, can achieve higher ammonia yields (*ca*. 35% overall).[8c] Understanding subtle factors that lead to productive reactivity at N_2 is essential to improving molecular nitrogen fixation catalysts.

We recently reported the utilization of a π-accepting cyclic (alkyl)(amino)carbene (CAAC)[15] to synthesize a structurally unusual 2-coordinate, formally L_2Fe^0 complex by reduction of its corresponding 2-coordinate Fe^I cation.[16] We reasoned that the polarizability of the CAAC ligand, by comparison to typical NHCs,[17] might better facilitate N_2 binding and productive functionalization. Note that low-valent Fe-carbene complexes[18] have to date been surprisingly resistant to N_2 binding, with the tripodal, N-heterocyclic carbene (NHC) containing, systems of Meyer[19] and Smith[20] underscoring this point. To our knowledge, a bis(imidazol-2-ylidene)pyridine scaffold is the only Fe-carbene derivative where N_2 binding has been established.[21] Here we show that the 2-coordinate $(CAAC)_2Fe$ complex binds N_2, but only at low temperature, and that this binding event exposes an otherwise unavailable 1-electron reduction step to form 3-coordinate $(CAAC)_2Fe(N_2)^-$ and desirable reactivity at the coordinated N_2.

Under an atmosphere of N_2, a solution of $(CAAC)_2Fe$ in pentane exhibited drastic changes in the absorption spectrum upon cooling at temperatures below −80 °C (Figure 2A). This temperature dependent change in the optical profile of $(CAAC)_2Fe$ under N_2 was reversible over several cooling-warming cycles. To confirm that the change in the optical spectrum was indeed related to the presence of N_2, the solution was thoroughly degassed by five freeze-pump-thaw cycles and variable temperature UV-vis spectra were re-collected (See SI Figure S7, right). In this case, the standard spectrum of $(CAAC)_2Fe$ was recovered. Re-exposing the solution to N_2 resulted in the previously observed temperature dependent profile. Thermodynamic parameters were extracted from a van't Hoff plot of the experimental data (See SI). As expected, binding of dinitrogen is exothermic (ΔH = −22.1 kcal mol^{-1}) and is associated with negative entropy (ΔS = −8.1 cal K^{-1} mol^{-1}). These parameters are similar to those recently reported for N_2 coordination at Co.[21] The N_2 binding constant at room temperature is very low (K_{eq} = 0.2), consistent with our initial report of a 2-coordinate $(CAAC)_2Fe$ complex.[16]

To structurally confirm the binding of dinitrogen at low temperature, we sought to trap the putative complex $(CAAC)_2Fe(N_2)$ (Scheme 1). The presence of an additional π-accepting ligand (N_2) facilitates the further reduction of $(CAAC)_2Fe^0$ to a formal Fe^{-I}. Hence, reduction of $(CAAC)_2Fe$ with KC_8 at −95 °C in diethyl ether in the presence of 18-crown-6 yielded, after work-up, dark brown crystals of $[(CAAC)_2Fe(N_2)]$ [K(18-crown-6)] in moderate yield (42%) (Scheme 1). Temperature control was crucial: reduction at room

temperature resulted instead in decomposition of the starting material to intractable products, and at −78 °C, only traces of $[(CAAC)_2Fe(N_2)]^-$ could be detected by IR spectroscopy. An XRD study of crystals of $[(CAAC)_2Fe(N_2)]$ [K(18-crown-6)] confirmed the binding of N_2 to a 3-coordinate Fe center in an end-on fashion with an additional ion-pair of the β-N-atom to the K(18-crown-6) cation (Figure 2D).

The structure of $[(CAAC)_2Fe(N_2)]$ [K(18-crown-6)] reveals a distorted trigonal planar Fe center (Σ_{angle} = 359.8°), with a very wide C-Fe-C angle (140.81(10)°). The C-N distances of the CAAC ligand are substantially elongated: they are 1.386(3) and 1.411(3) Å, compared with 1.315(3) Å for the free ligand.[15c] This C-N lengthening is indicative of a substantial amount of spin leakage from the highly reduced Fe center to the supporting CAAC ligand.[16] Complex $[(CAAC)_2Fe(N_2)]$ [K(18-crown-6)] represents a rare example of a structurally characterized pseudo-terminally bonded, 3-coordinate Fe-N_2 complex.[13,14]

A sharp band was observed in the IR spectrum of $[(CAAC)_2Fe(N_2)]$[K(18-crown-6)] at 1850 cm^{-1} (ATR-IR; thin film), attributed to the ν_{NN} stretch. This value is higher in energy than the transiently observed $[\beta\text{-diketimidatoFe}(N_2)]_2Mg(thf)_4$ species reported by Holland and co-workers (1818 cm^{-1}),[13] but lower than other anionic terminal Fe-N_2 complexes where the Fe center resides in higher coordination numbers (1905 – 1927 cm^{-1}).[9,10a] As expected for a formal Fe^{-I} species, a room temperature solution magnetic moment for $[(CAAC)_2Fe(N_2)]$[K(18-crown-6)] of 1.9μ_B in C_6D_6 was measured, consistent with its frozen glass (Et_2O) EPR spectrum (Figure 2B, a) and indicative of an S = 1/2 ground state.

Exposure of $[(CAAC)_2Fe(N_2)]$[K(18-crown-6)] to trimethylsilylchloride in diethyl ether resulted in a rapid color change from dark brown-red to dark green. A diagnostic broad band at 1675 cm^{-1} was observed in the IR spectrum of the crude reaction mixture, reminiscent of previously observed ν_{NN} stretches for Fe-silyldiazenido complexes.[9,10a] The presumed diazenido product $(CAAC)_2Fe(N_2SiMe_3)$ rapidly decomposed upon attempted work-up to the $(CAAC)_2Fe$ complex. A bulkier silylating reagent led to a more stable product. Hence, a similar change of color from dark brown-red to dark green was observed when triethylsilylchloride was added to the $[(CAAC)_2Fe(N_2)]$[K(18-crown-6)] complex (Scheme 1). The diazenido product, $(CAAC)_2Fe(N_2SiEt_3)$ was isolated as an analytically pure, dark green solid in moderate yield (52%). Its IR spectrum exhibits a broad band at 1690 cm^{-1}. Complex $(CAAC)_2Fe(N_2SiEt_3)$ is high spin S = 3/2 (room temperature solution magnetic moment of 3.9μ_B), consistent with its frozen glass EPR spectrum at 10 K showing broad signals at low field (Figure 2B, b). Its electronic structure is therefore distinct from previously characterized 5-coordinate $XL_3Fe(N_2SiR_3)$ species that are low spin. For instance, $(TP^{iPr}B)Fe(N_2SiMe_3)$ is an S = 1/2 species.[9b]

The ^{57}Fe Mössbauer spectra of $[(CAAC)_2Fe(N_2)]$[K(18-crown-6)] and $(CAAC)_2Fe(N_2SiEt_3)$ were recorded at 80 K in the solid state (Figure 2C). Fits to the data provided isomer shifts at δ = 0.56 and δ = 0.59 mm s^{-1}, respectively, with quadrupole splitting of ΔE_Q = 1.67 and ΔE_Q = 1.60 mm s^{-1}. The isomer shift value is in line with previously reported 3-coordinate bis-carbene Fe complexes.[16,24] For example, $(CAAC)_2FeCl$ has an isomer shift of 0.52 mm s^{-1}. The spectrum of $[(CAAC)_2Fe(N_2)]$[K(18-crown-6)] displays an asymmetrical doublet presumably caused by anisotropy in the polycrystalline sample.[25] A minor

component (~9% of the total Fe content), whose parameters fit the oxidation product $[(CAAC)_2Fe]^+$,[16] was also detected (Figure 2C, a).

In previous studies of 5-coordinate Fe-N_2 species, we have empirically determined that the ability to successfully silylate the β-N-atom of an Fe-N_2 derivative can translate to efficacy of the system towards reductive protonation.[9c,10] Attempts to fix N_2 to NH3 at room temperature using $(CAAC)_2Fe$ in the presence of excess KC_8 and $HBAr^F{}_{24}{\cdot}2Et_2O$ in diethyl ether, regardless of the order of addition, proved largely ineffective (Table 1; See SI Figure S12). This observation is consistent with a very limited degree of N_2 binding to $(CAAC)_2Fe$ at room temperature, and the requirement that a $(CAAC)_2Fe(N_2)$ species be present to facilitate N_2 fixation. Indeed, when $(CAAC)_2Fe$ was treated at −95 °C with an excess of KC_8 (50 eq), followed by an excess of $HBAr^F{}_{24}{\cdot}2Et_2O$ (50 eq), the formation of 3.3 ±1.1 equivalents of NH_3 per Fe center was observed. Similar yields (3.4 ±1.0 eq) were obtained employing the 2-coordinate Fe(I) cation $[(CAAC)_2Fe][BAr^F{}_{24}]$ under the same conditions at −95 °C. The enhancement of the N_2-to-NH_3 reduction yield at very low temperature correlates with the variable temperature optical data for $(CAAC)_2Fe$, which shows that N_2 binding to $(CAAC)_2Fe$ becomes favorable only at low temperature. Indeed, the yield of NH_3 is negligible at −50 °C (0.3 eq) and is still quite low at −78 °C (0.9 eq). Note that significantly lower temperature (−113 °C) was examined but did not improve the NH_3 yield beyond that obtained at −95 °C.

Although these NH_3 yields are low compared with our two previously reported Fe catalysts[10] Schrock's original Mo system,[4] and especially Nishibayashi's recently improved Mo system,[5a] $(CAAC)_2Fe$ is nevertheless a very modest catalyst for nitrogen fixation to ammonia and the yields of NH_3 per Fe equivalent reported here are far greater than those that have been observed for previously studied 3-coordinate Fe-N_2 complexes (< 0.2 eq per Fe), including $[\beta\text{-diketimidatoFe}(N_2)]_2Mg(thf)_4$ species (Figure 1).[13] We speculate that the ability of $(CAAC)_2Fe$/$(CAAC)_2Fe(N_2)$ to perform nitrogen fixation may arise from the relative flexibility of the system, capable of switching between 2- and 3-coordinate geometries, and allowing for the formation of highly covalent Fe-N_x multiple-bond interactions. The recent isolation of a 3-coordinate Fe-bis(imide) complex supported by CAAC by Deng and co-workers is noted in the latter context.[26]

For comparison, we also explored $(CAAC)_2Fe$ in the context of catalytic N_2 silylation. Catalytic silylation reactions of N_2 under strongly reducing conditions have been known for many years using metals such as Cr,[27] Ti[28] and Mo,[29] and recently, such silylations were extended to systems using Fe pre-catalysts including $Fe(CO)_5$ and Cp_2Fe.[30] For example, $Fe(CO)_5$ was shown to produce up to 25 equivalents of $N(SiMe_3)_3$ per Fe in the presence of a vast excess sodium metal and TMSCl at room temperature.[30] These silylation reactions remain mechanistically ill-defined. Only trace yield of $N(SiMe_3)_3$ could be detected using Nishibayashi's conditions (Na as reductant, in THF)[30] with $(CAAC)_2Fe$ as pre-catalyst. However, when a catalytic amount of $(CAAC)_2Fe$ was instead treated with a large excess of KC_8 (600 eq) and trimethylsilylchloride (600 eq), the formation of 24.4 ± 2.7 equivalents of $N(SiMe_3)_3$ was observed (See Table S1 in the SI for details). Slightly lower TONs (19.4 ±3.0) were obtained using $(CAAC)_2FeBAr^F{}_{24}$ as a pre-catalyst instead. The catalytic activity was significantly reduced (7.0 ±1.0) when the reaction was performed at

−78 °C. The attenuation in $N(SiMe_3)_3$ product is presumably related to slower generation of trimethylsilyl radical at low temperature.

Although it is presently unclear what the mechanistic requirements are for the N_2-to-$N(SiMe_3)_3$ catalysis mediated by various Fe precursors including $(CAAC)_2Fe$, the N_2-to-NH_3 chemistry described herein appears to require a well-defined molecular Fe-N_2 species. Indeed, significant N_2-to-NH_3 conversion is observed only at the low temperatures where N_2 binds $(CAAC)_2Fe$ sufficiently favorably. The low-temperature N_2 binding event facilitates subsequent electron-transfer, evidenced by the very low temperature required to synthetically reduce $(CAAC)_2Fe(N_2)$ and isolate highly reactive $[(CAAC)_2Fe(N_2)]^-$.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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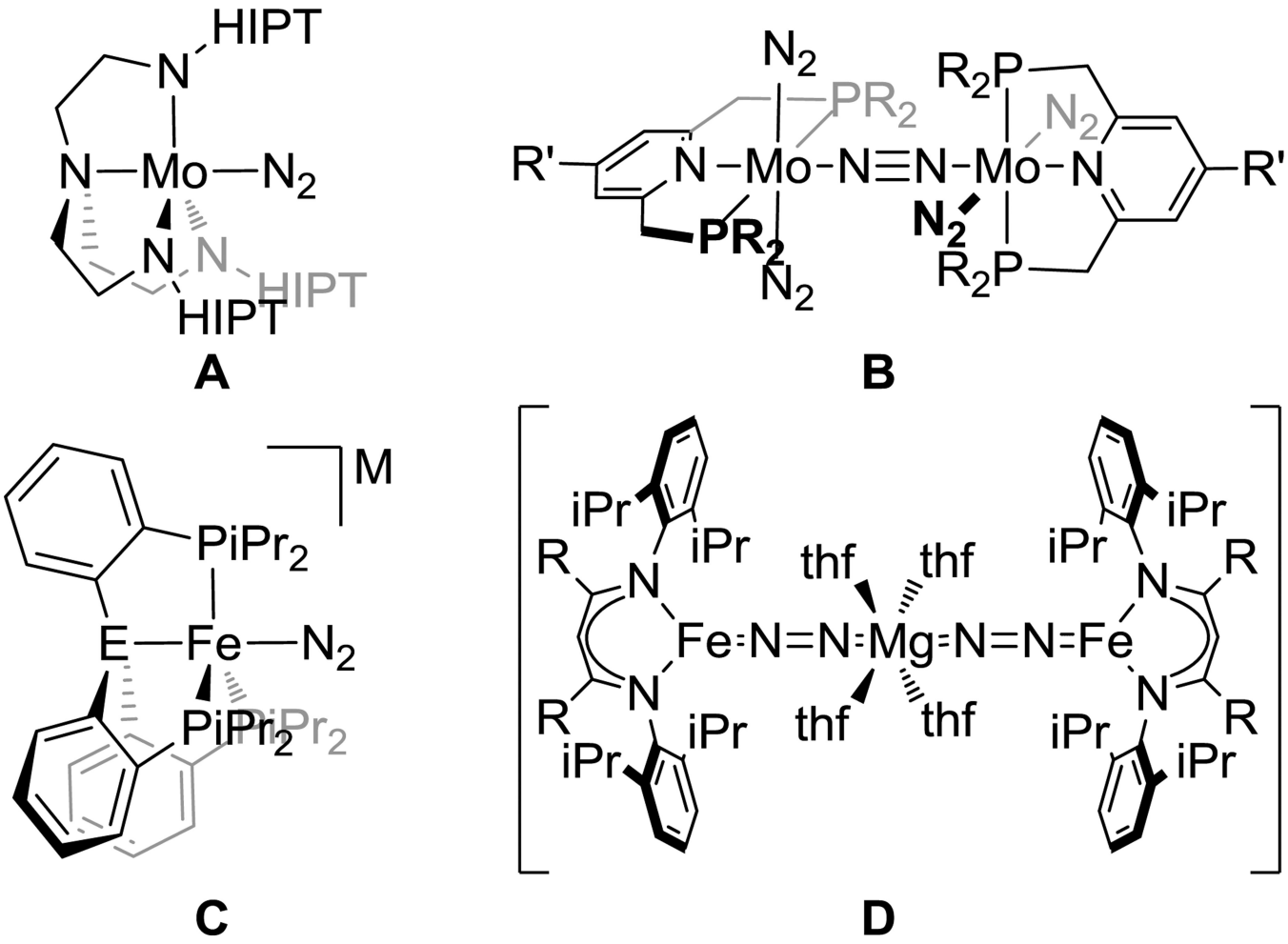


Figure 1.

Representative Mo and Fe complexes studied for catalytic N_2 reduction to NH_3. R = tBu; R' = H, OMe; HIPT = hexaisopropylterphenyl; E = B, C; M = K, Na.

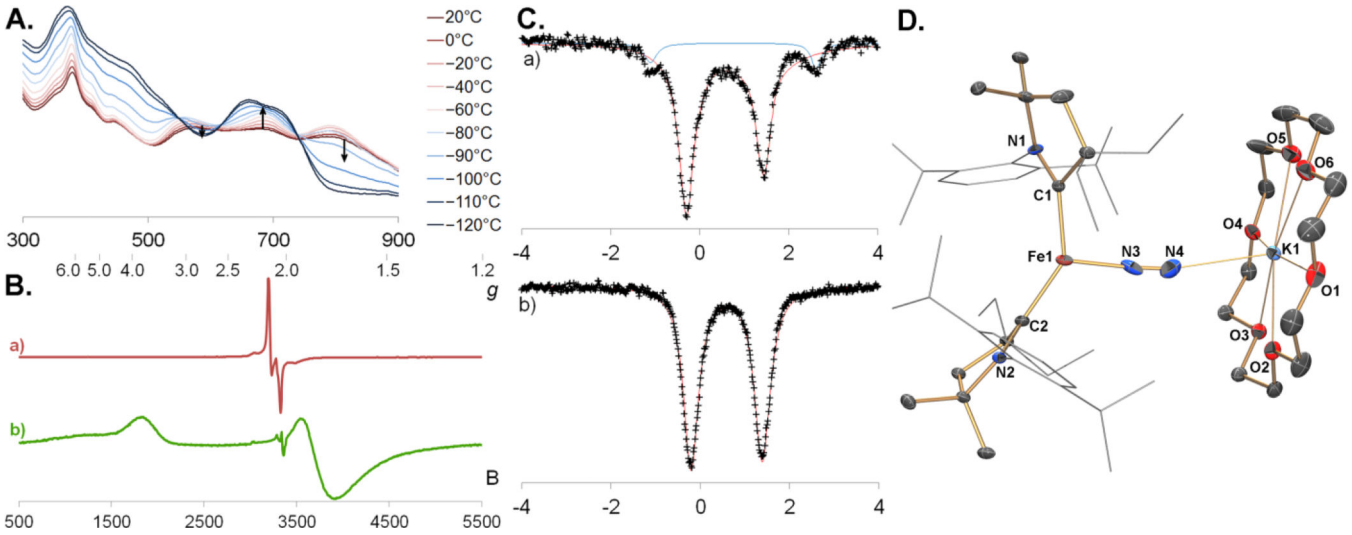
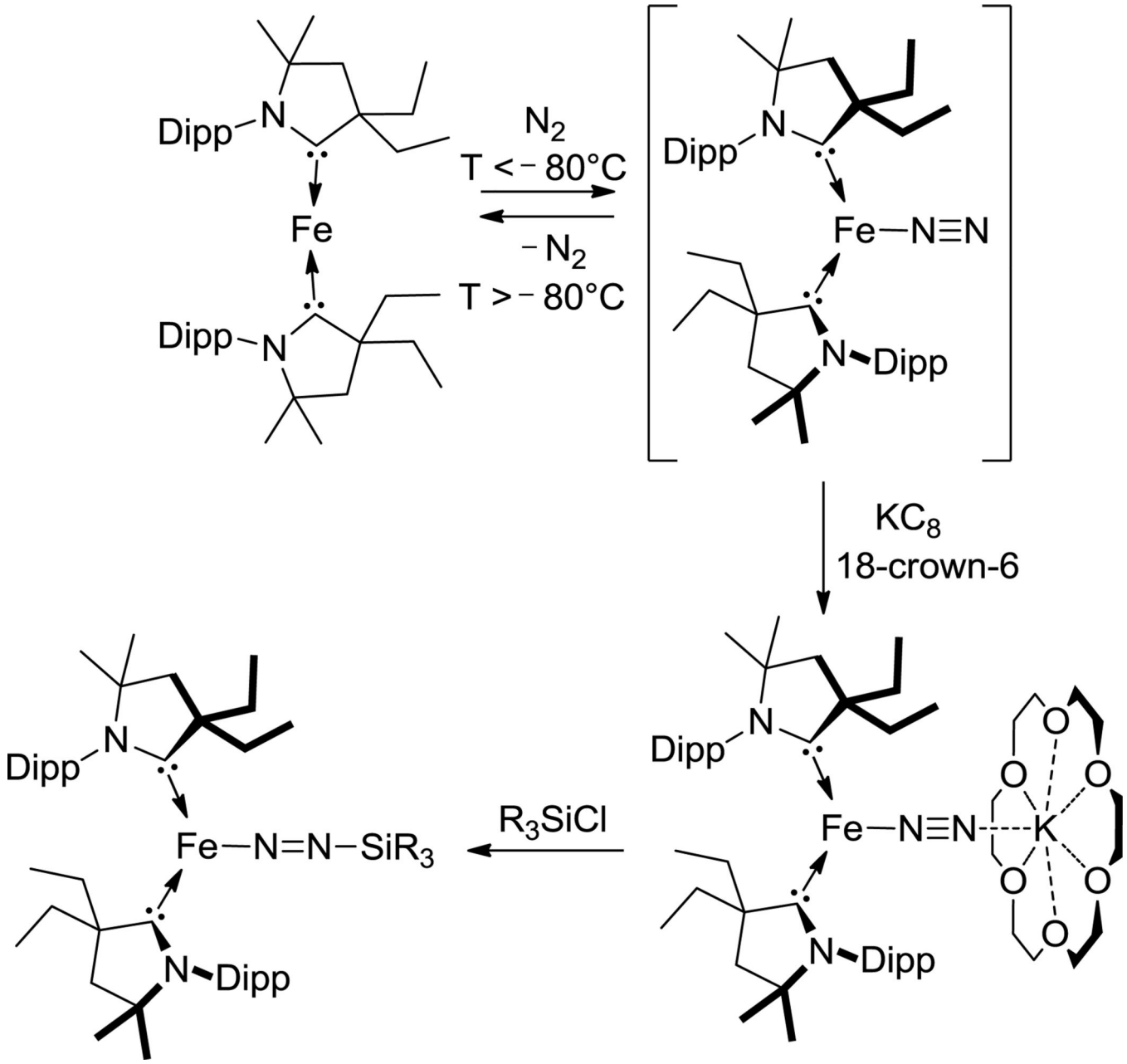


Figure 2.

A. Variable temperature UV-vis spectra of $(CAAC)_2Fe$ in a pentane solution. a) under N_2 atmosphere; b) under vacuum. **B**. X-Band EPR spectra at 10 K: a) $[(CAAC)_2Fe(N_2)][K(18\text{-crown-6})]$ in a frozen Et_2O glass; b) $(CAAC)_2Fe(N_2SiEt_3)$ in a frozen methylcyclohexane glass. **C**.^{57}Fe Mössbauer spectra for microcrystalline samples obtained at 80 K in boron nitride pellets. a) $[(CAAC)_2Fe(N_2)][K(18\text{-crown-6})]$; b) $(CAAC)_2Fe(N_2SiEt_3)$. Solid red lines correspond to the simulated data. Solid blue line in a) correspond to a minor species (~ 9% of Fe) parameters of $\delta = 0.74$ mm s^{-1} and $\Delta E_Q = 3.79$ mm s^{-1}. **D**. Structure of $[(CAAC)_2Fe(N_2)][K(18\text{-crown-6})]$ in the solid state. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.[23] Selected bond lengths (Å) and angles (°): C1–Fe1 = 1.924(2), C2–Fe1 = 1.919(2), C1–N1 = 1.386(3), C2–N2 = 1.411(3), Fe1–N3 = 1.778(3), N3–N4 = 1.035(4), N4–K1 = 2.726(4); C1–Fe1–C2 = 140.81(10), C1–Fe1–N3 = 101.91(11), C2–Fe1–N3 = 117.08(11), Fe1–N3–N4 = 175.5(3).

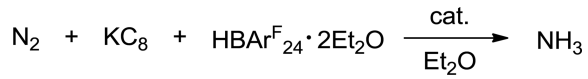


Scheme 1.

Reduction of $(CAAC)_2Fe$ and subsequent trapping with silylating reagents. Dipp = 2,6-diisopropylphenyl; R = Me, Et.

Table 1

Catalytic reduction of N_2 to NH_3[a]



Run	Catalyst	T	Eq NH3 per Fe
1	$(CAAC)_2Fe$	−113 °C	3.0 ±0.7
2	$(CAAC)_2Fe$	−95 °C	3.3 ±1.1
3	$(CAAC)_2Fe$	−78 °C	0.9 ±0.3[b]
4	$(CAAC)_2Fe$	−50 °C	0.3 ±0.2[b]
5	$(CAAC)_2Fe$	23 °C	0.4 ±0.2[b]
6	$(CAAC)_2FeBAr^F{}_{24}$	−95 °C	3.4 ±1.0
7	$(CAAC)_2FeN_2K(18\text{-}c\text{-}6)$	−95 °C	2.6 ±0.6
8	CAAC[c]	−95 °C	< 0.1
9	None	−95 °C	< 0.1

[a] Catalytic conditions: catalyst: 0.002 mmol, KC_8: 0.1 mmol, $HBAr^F{}_{24}{\cdot}2Et_2O$: 0.1 mmol, Et_2O, 45 min; yields are an average of 8 independent runs.

[b] Average of 4 runs.

[c] 0.004 mmol of CAAC used.